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Title: Photoenergy Transfer in SWCNT Mesomaterials

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# Photoenergy Transfer in SWCNT Mesomaterials

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Duque**

Los Alamos National Laboratory, Los Alamos NM

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- Sandia: CINT Core
  - Gabriel Montano
  - Yongming Tian



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Unclassified



# Introduction to SWCNTs

All Carbon nano-objects

Thermal  
Physical  
Optical  
Electronic

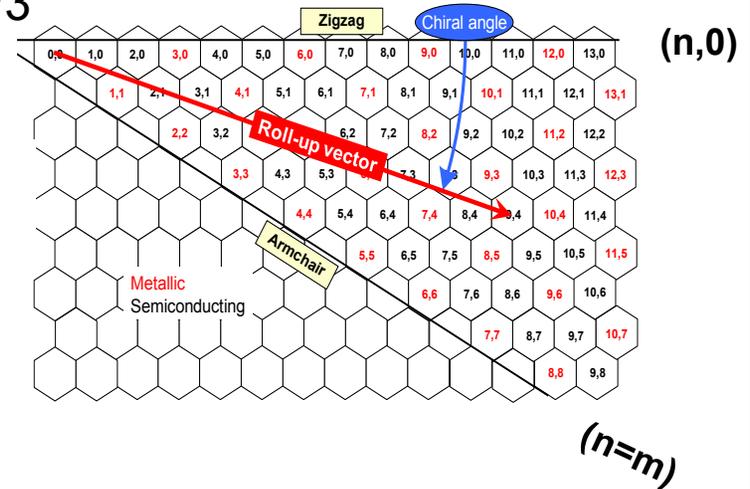
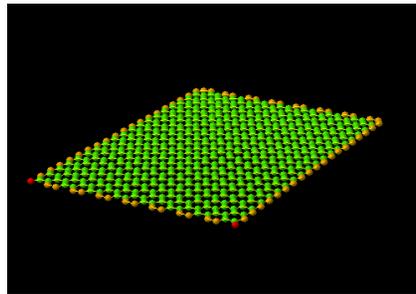
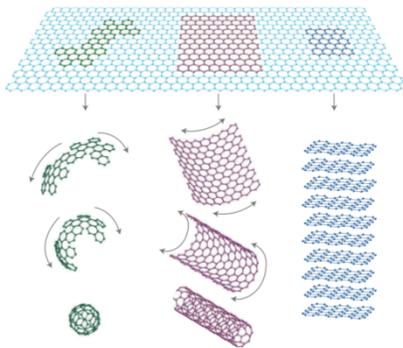
Improve mechanical strength  
Ideal for sensing and electrical circuits

Depending on their chirality can be

Metallic  
Semimetallic  
Semiconductors

$$(n-m)/3$$

(n,0) and (0,m): zig-zag  
(n,n): armchair



Chirality-dependence

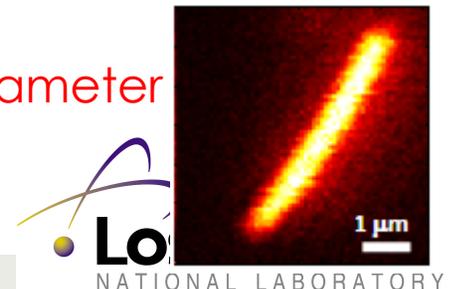
near-IR luminescence

o Bandgap proportional to diameter

O'Connell et al., Science (2002)  
Bachilo et al., Science (2002)  
Baughman et al., Science, (2002)  
Geim, A. K.; et al, Nat. Mater. (2007)

Cognet et al., Science (2007)  
Rao et al., Science (1997)  
Bonard, J. M., et al A. Appl. Phys. Lett., (1998)  
Niyogi et al., J. Am. Chem. Soc., (2007)

Unclassified



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# Environment Effects

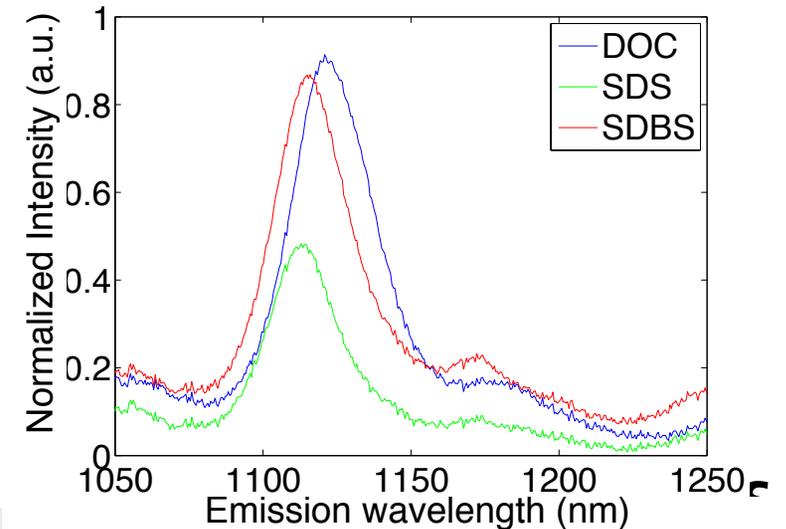
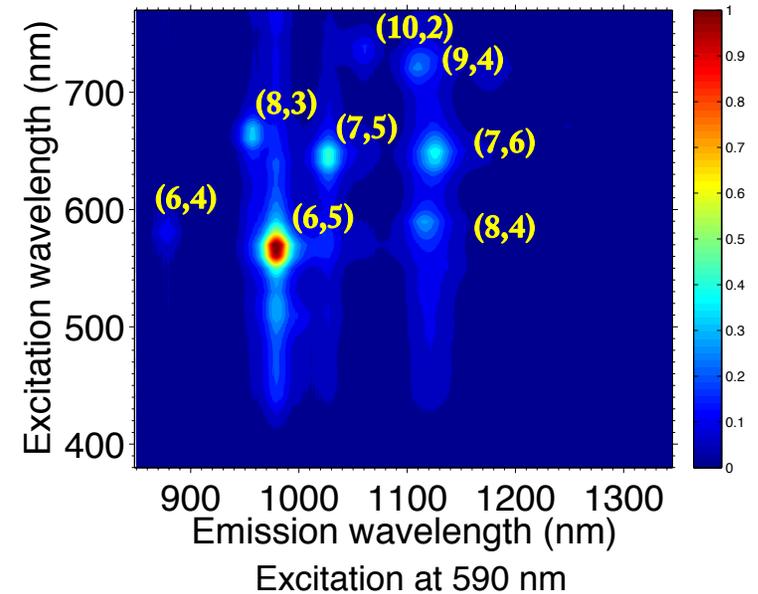
- Isolated SWCNTs fluoresce in near-IR

(n,m)	E11 (eV)	E22 (eV)
(6,4)	1.420	2.146
(6,5)	1.270	2.190
(7,5)	1.211	1.921
(7,6)	1.107	1.914
(8,3)	1.303	1.863
(8,4)	1.116	2.105
(9,4)	1.127	1.716
(10,2)	1.177	1.683

- Peak position and line-width dependent on dielectric isolation

$$\delta E_{\text{abs}}(\epsilon_1 \epsilon_2) \approx 43(\epsilon_1^{-1.6} - \epsilon_2^{-1.6}) \text{ meV}$$

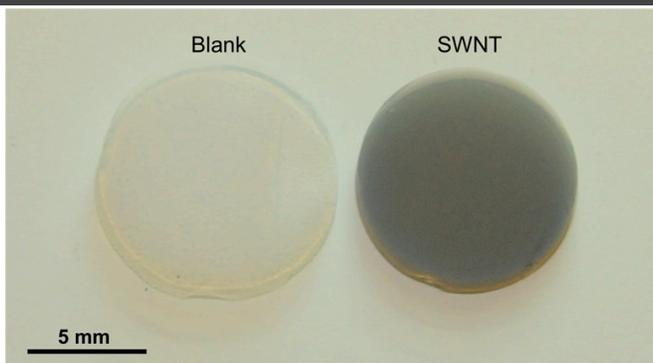
HiPco Batch 195.2 in SDBS



# Motivation

- CNT photovoltaics
  - Efficient charge and energy transport conduits
  - Exhibit very efficient exciton dissociation
  - Free carriers with very long lifetimes
  - Poor resonant absorption at low-Vis and UV-region.
- Dye-sensitized systems will enhance photovoltaic applicability however, need to understand CNT interactions with other materials in terms of energy and charge flow
- A model system for addressing this need is to probe porphyrin/CNT interactions
- Aerogels offer an avenue to probe interactions while varying the dielectric environment

# Mesomaterial Process

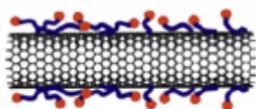


Density: ~ 60 mg/mL  
Surface Area: 1400 m<sup>2</sup>/g  
Pore Size: ~ 6 nm

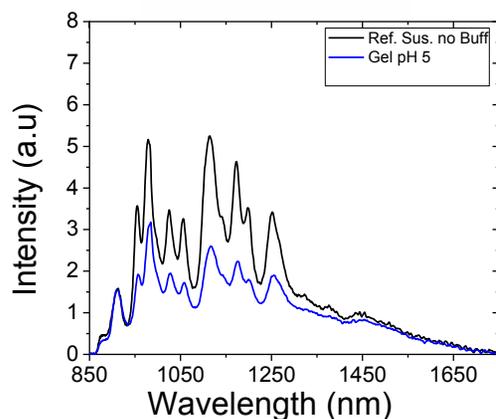
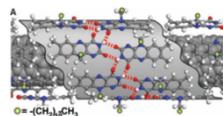
Highly adjustable SWCNT loading.

**High optical quality.**

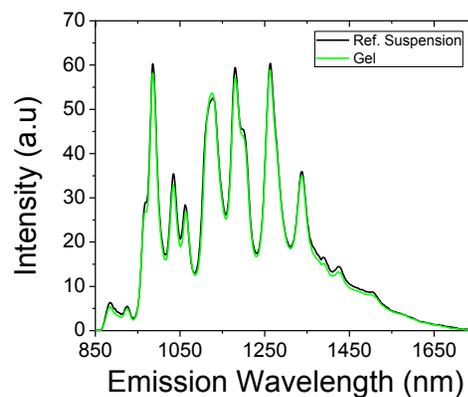
**SDS**



**DOC**



Loosely packed surfactant structure



Ordered surfactant structure

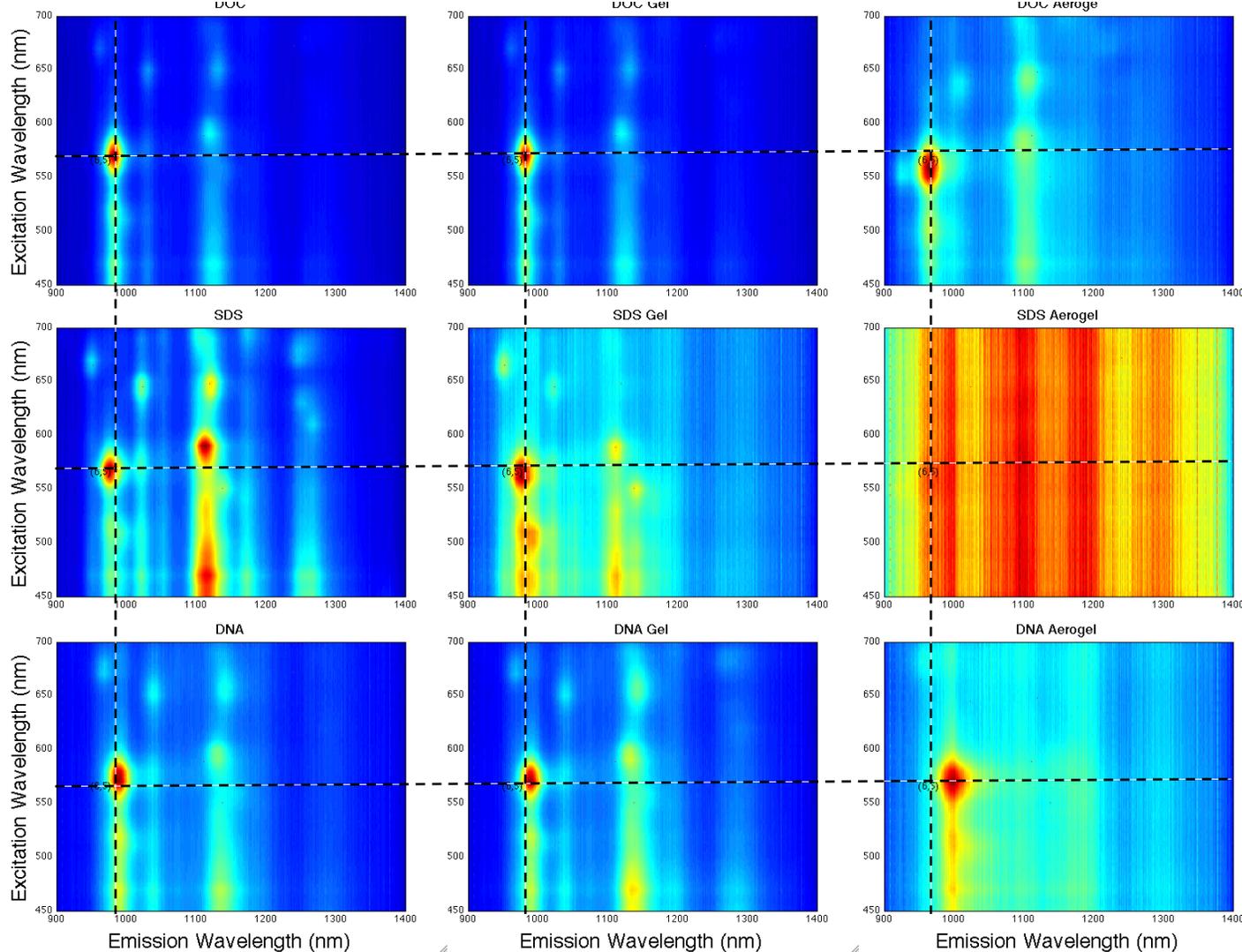
- Biocompatible
- Inert
- Highly permeable
- Tunable interfacial characteristics

# SWCNT Aerogels

## Suspensions

## Wet Gels

## Aerogels



## After Aerogel

DOC

Blueshift in  
emission and  
excitation

SDS

Very low  
emission  
Small blueshift  
Strong interaction  
with matrix

DNA

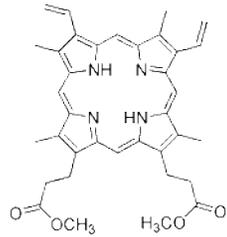
Blueshift in  
excitation (10nm)  
but redshift in  
emission (10nm)

Unclassified

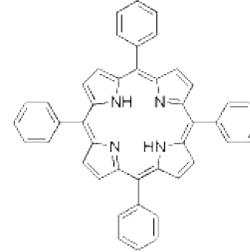
# Porphyrin Tunability



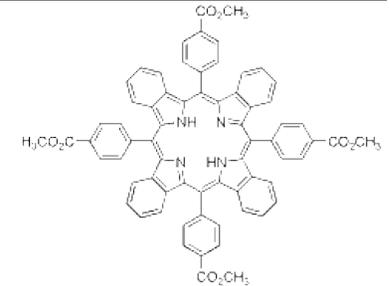
Porphin



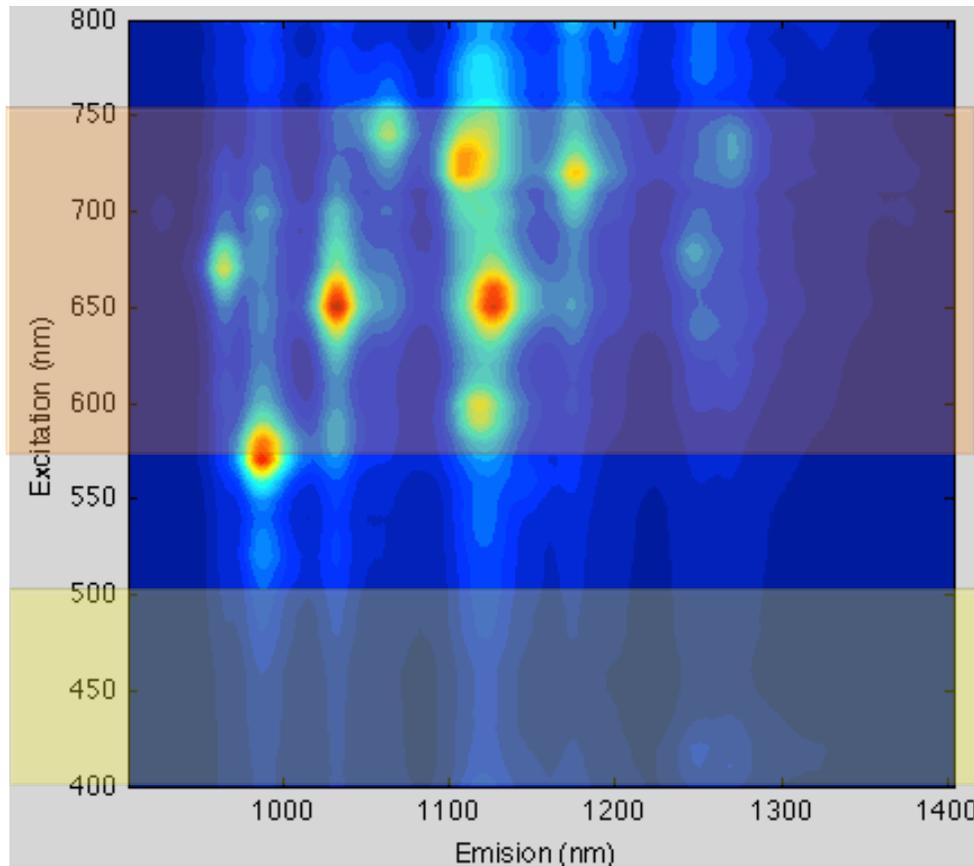
PPIX



TPP



TBP construct



Name	Soret (nm)	Q1 (nm)
Porphin	395	616
PPIX	408	633
TPP	419	650
ZNTPP	423	595
TBP construct	470	726

Unclassified

# Porphyrin Injection

**Table 1.** Spectral Changes of Surfactant-Coated SWNTs Mixed with Organic Solvents

organic solvent	dielectric constant <sup>a</sup>	dipole moment (D) <sup>a</sup>	SDBS–SWNTs		SDS–SWNTs	
			fluorescence intensity change	solvatochromic shift change	fluorescence intensity change	solvatochromic shift change
hexane	1.89	0	small increase	blue	large decrease	red
benzene	2.28	0	varied	red	large increase	slight blue
chloroform	4.81	1.04	decrease	red	varied	varied
ODCB	10.12	2.50	decrease	red	large decrease	red
water	80.1	1.85	—	—	—	—

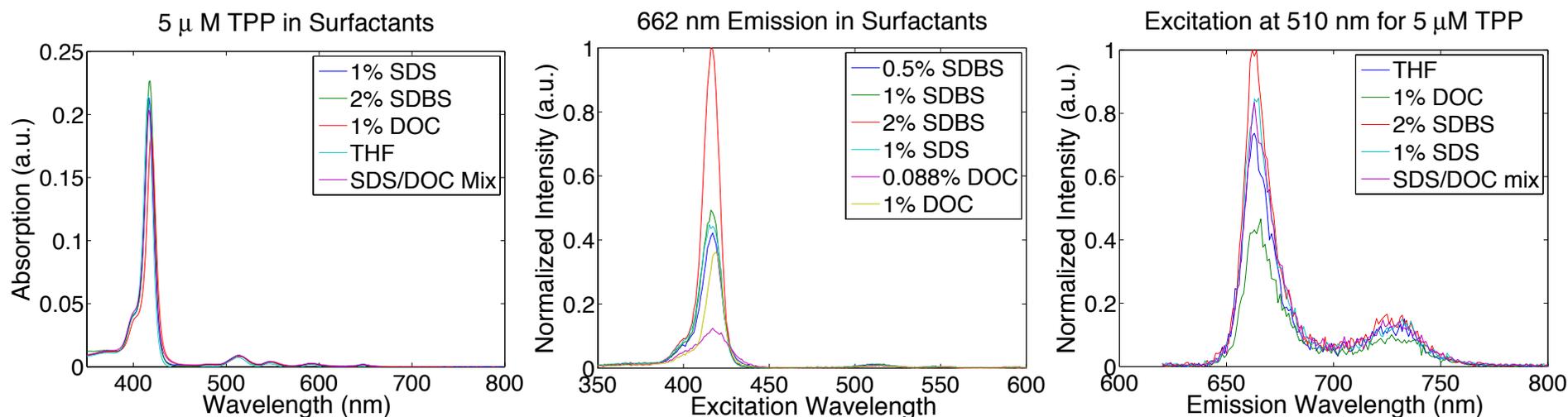
<sup>a</sup> Values taken from the CRC Handbook of Chemistry and Physics.

- Disperse water insoluble porphyrin with THF
- Disperse SWCNTs with surfactant in aqueous solution
- Mix minimal THF/porphyrin solution with SWCNT/surfactant dispersion
  - Heat or sonication is needed to enhance porphyrin injection into micelles

Wang et al., *J. Am. Chem. Soc.* (2008)  
Casey et al., *J. Mater. Chem.* (2008)  
Roquelet et al., *Appl. Phys. Lett.* (2010)

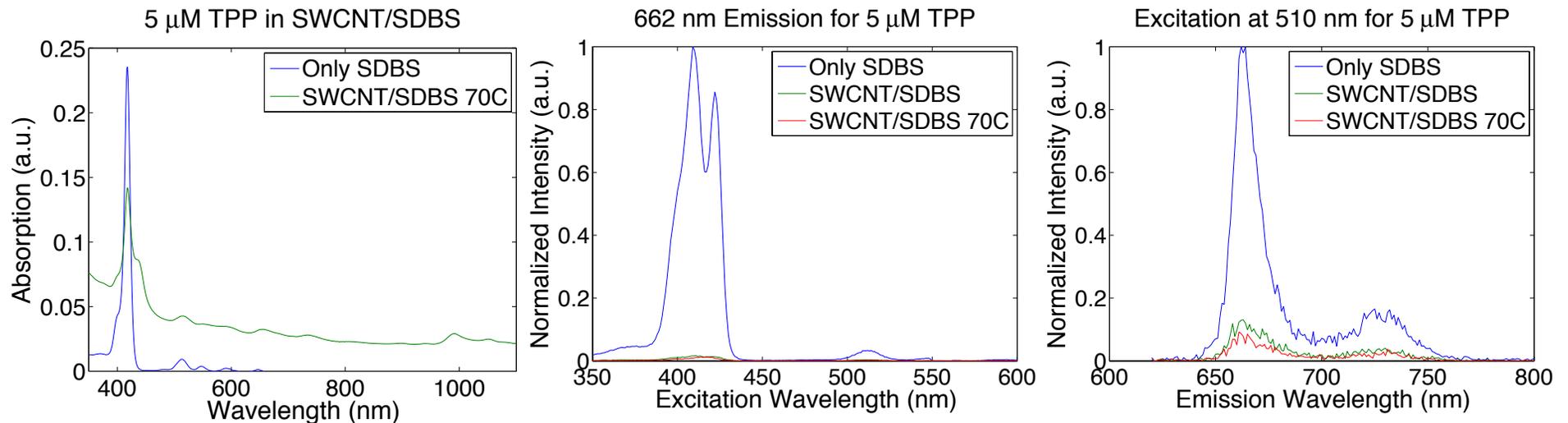
Unclassified

# Surfactant Concentration



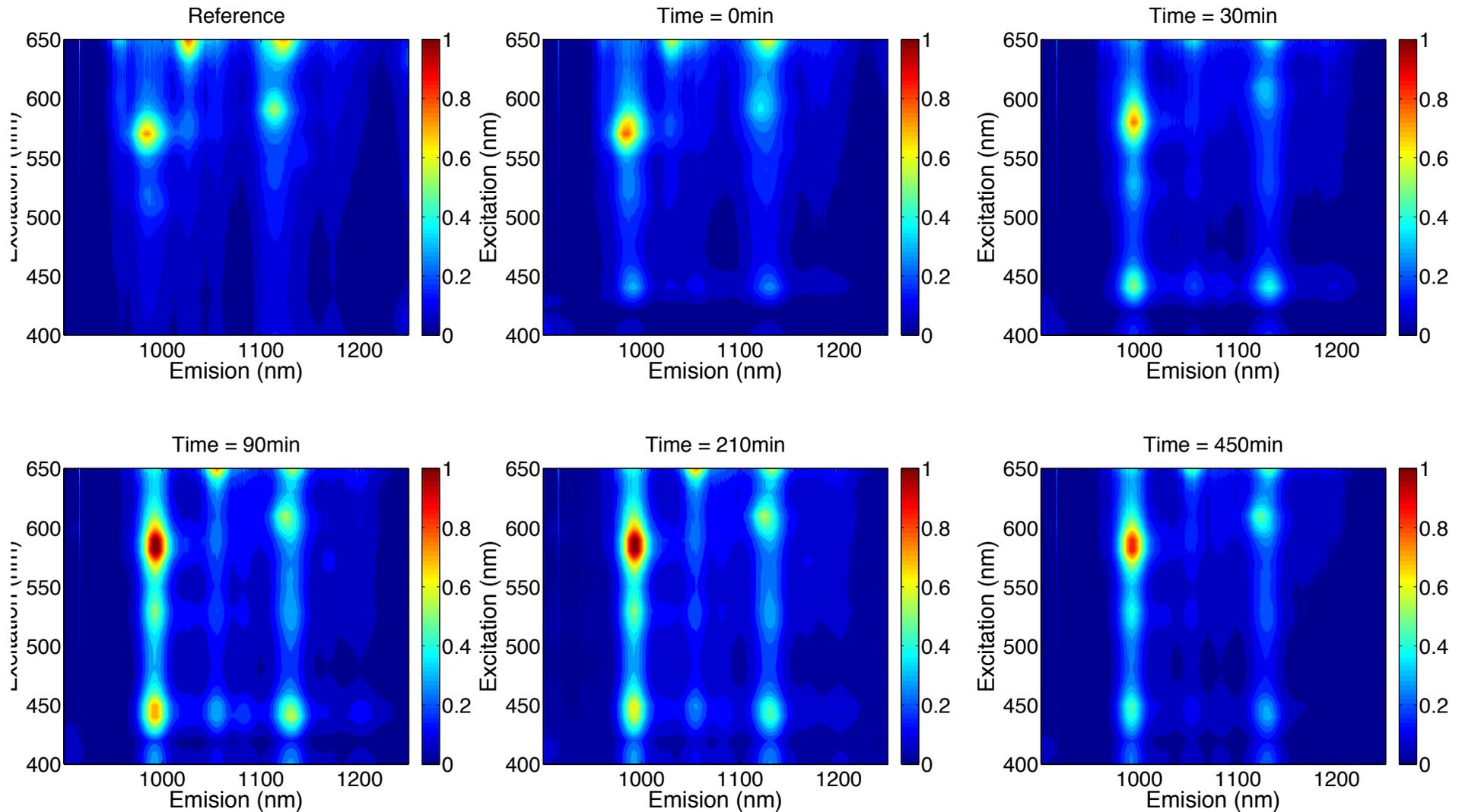
- No evidence of aggregation in absorbance
- Variation in Emission dependent on surfactant type and concentration.
  - Soret band is more affected than Q-band.
- 2% SDBS shows the greatest emission suggesting greatest amount of free porphyrin within micelles

# Porphyrin with SWCNTs



- New absorption peak at 440 nm appears when interacting with SWCNTs.
- Porphyrin fluorescence is significantly quenched when SWCNTs are present.

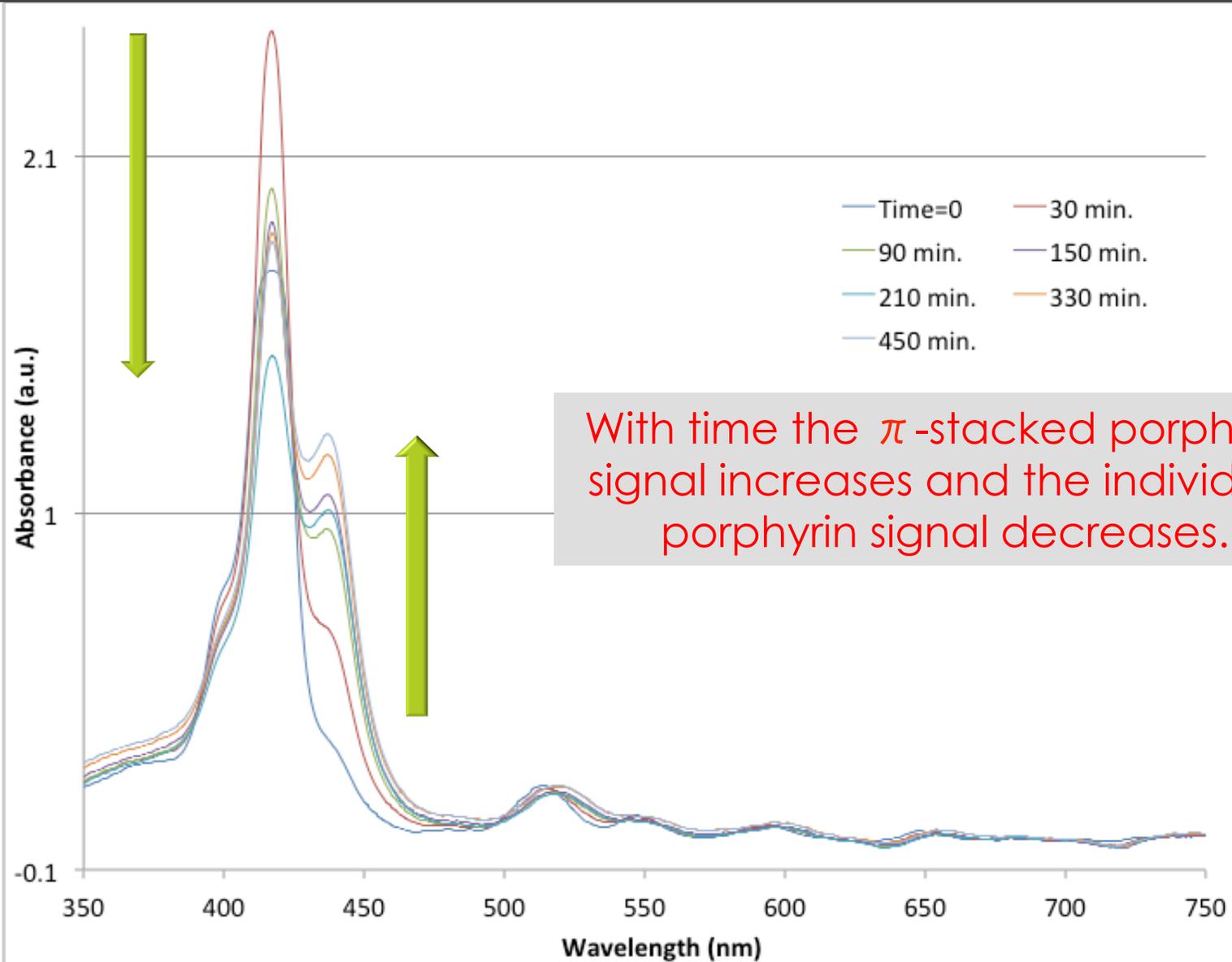
# Heating Time



Unclassified

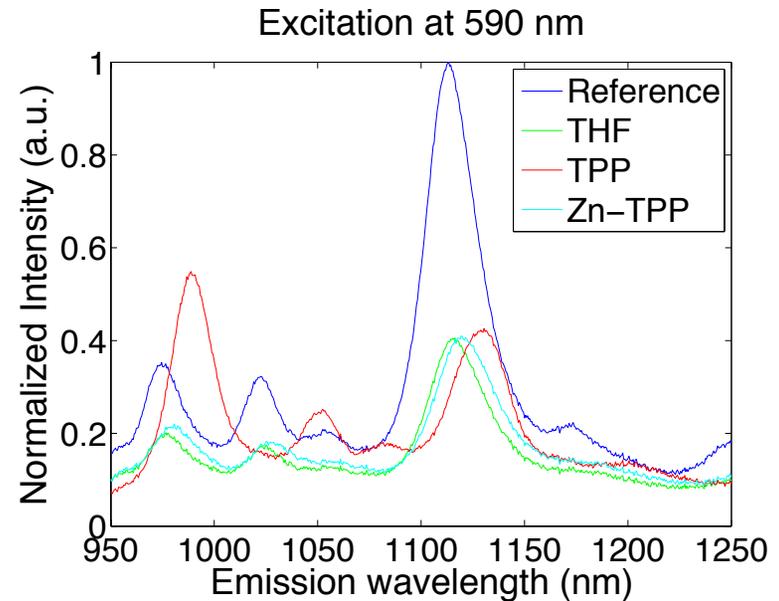
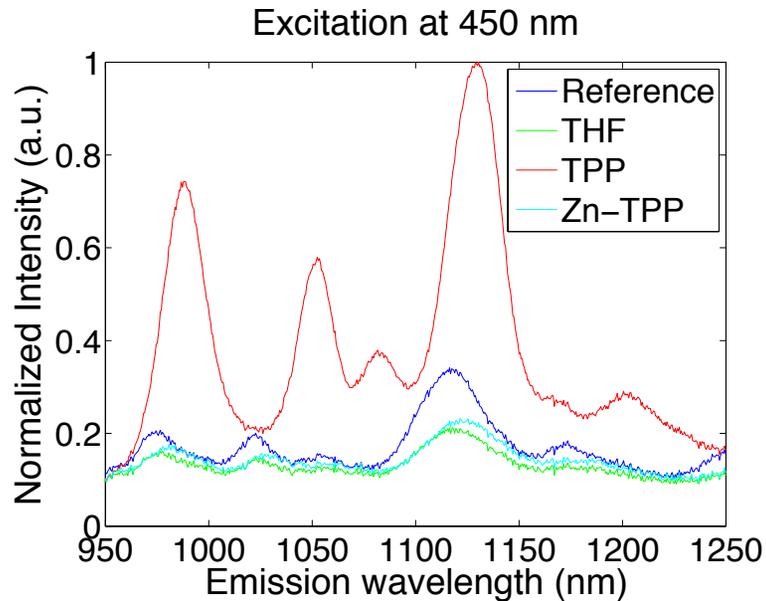


# Porphyrin Absorption



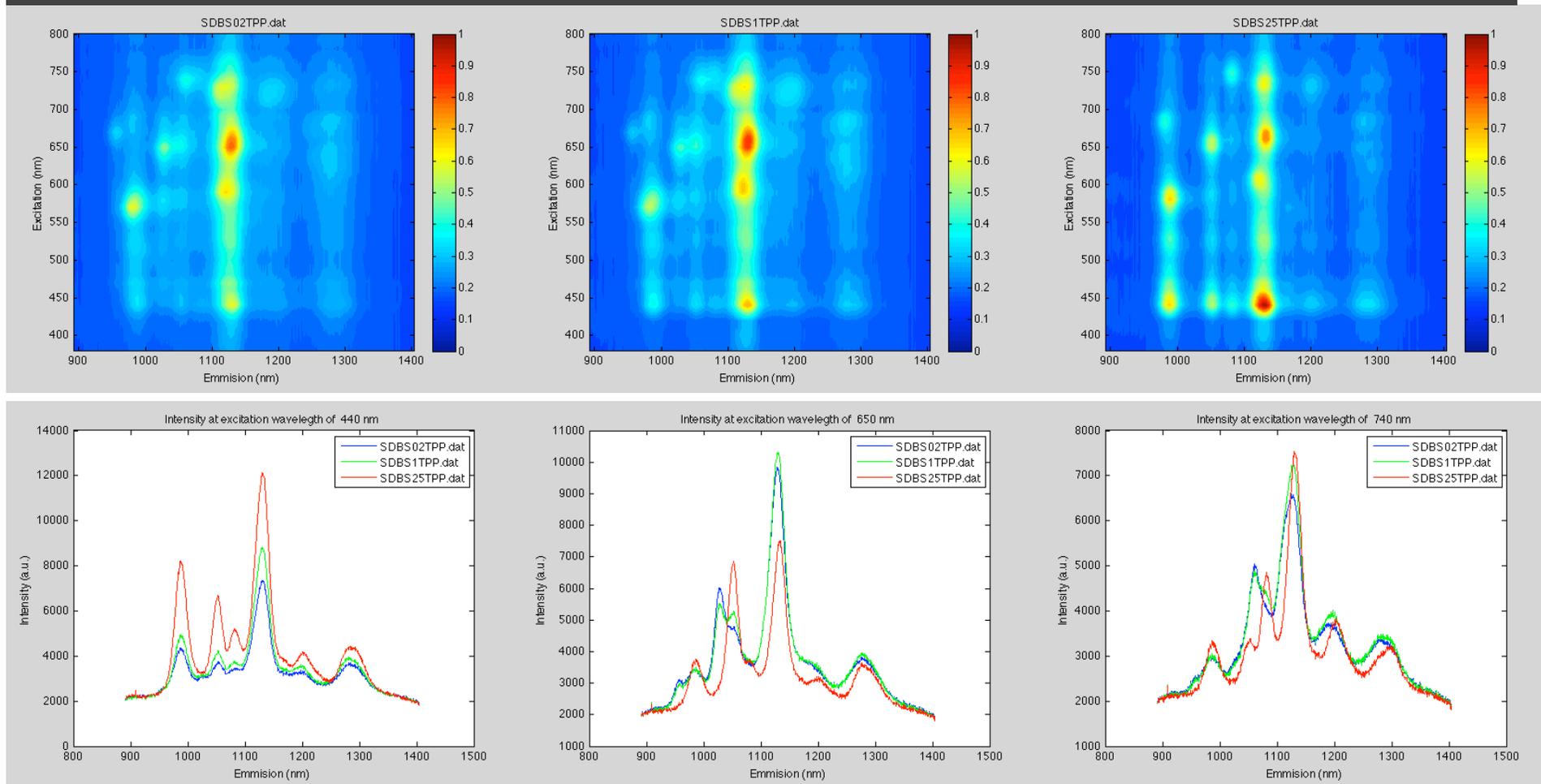
With time the  $\pi$ -stacked porphyrin signal increases and the individual porphyrin signal decreases.

# Shifts in SWCNTs



- Fluorescence from SWCNTs at 450 nm excitation, where SWCNTs normally have no fluorescence
  - Porphyrin absorbing and transferring energy to SWCNT which then fluoresces
- Significant shift in SWCNT emission with porphyrin interaction.
  - TPP shows greater shift than Zn-TPP corresponding to the greater energy transfer peak at 450 nm

# SDBS Concentration



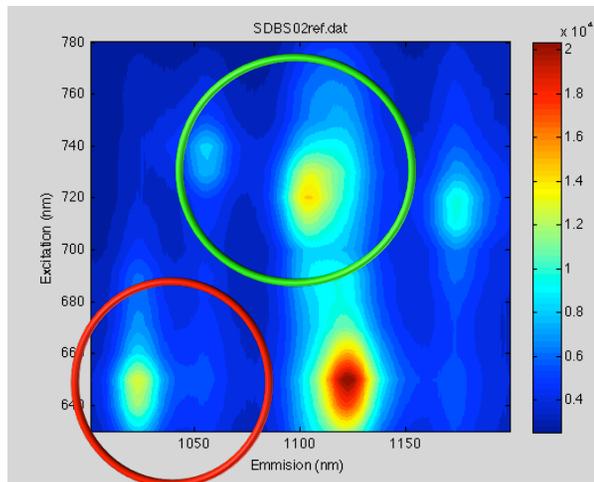
- Greater SDBS concentration has greater energy transfer due to greater isolation of porphyrin.
- At 1% SDBS there seems to be two species of SWCNTs, with and without porphyrin interaction.

# SWCNT Shifts

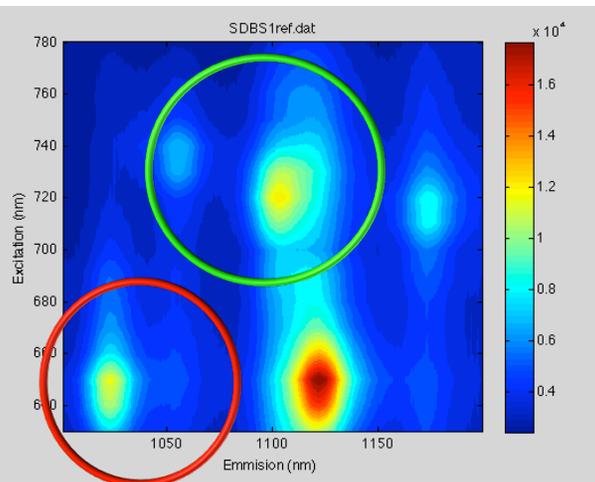
0.2% SDBS

1% SDBS

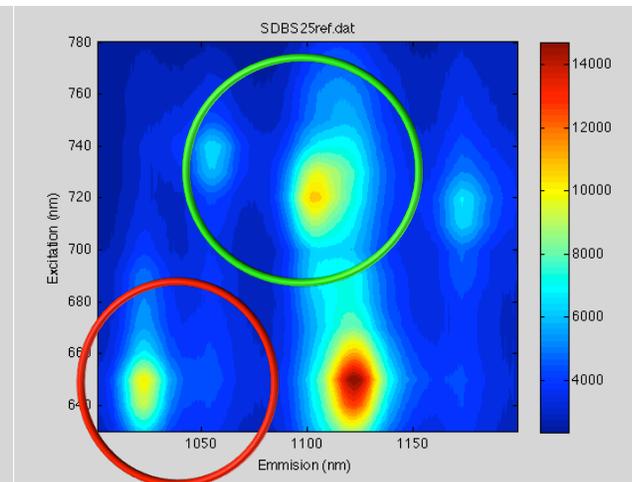
2.5% SDBS



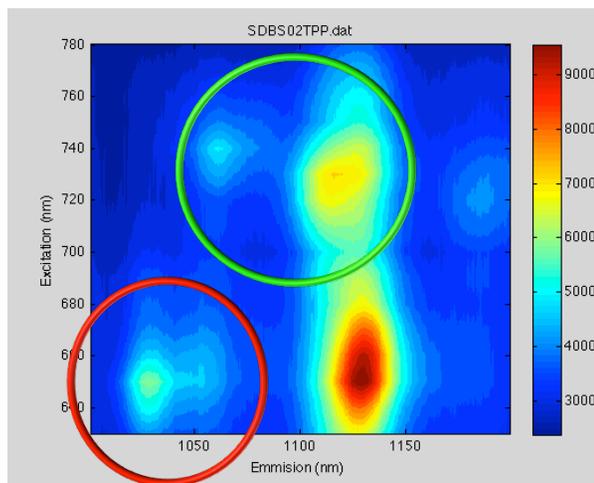
ref



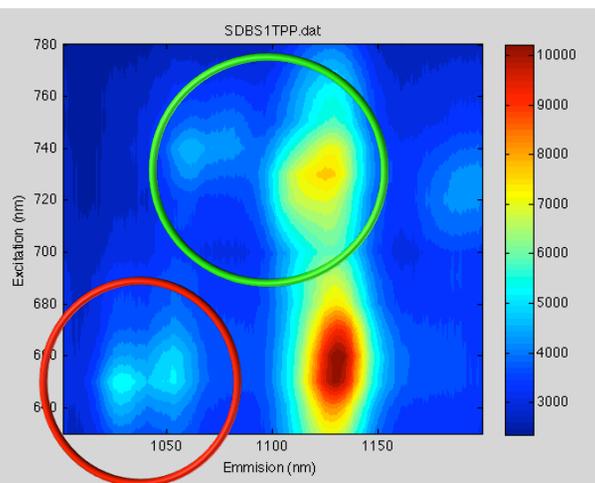
ref



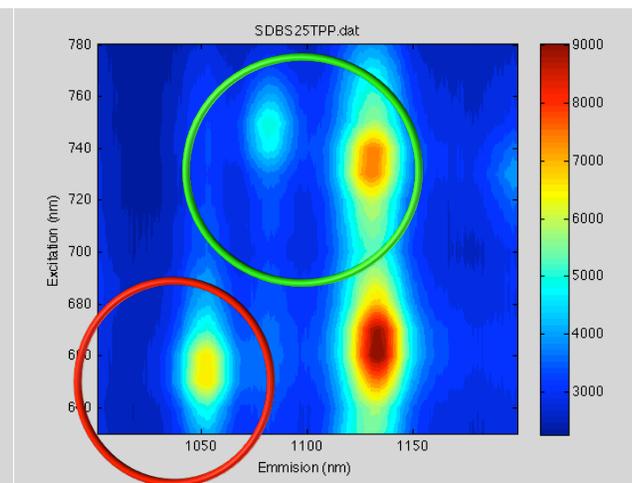
ref



TPP



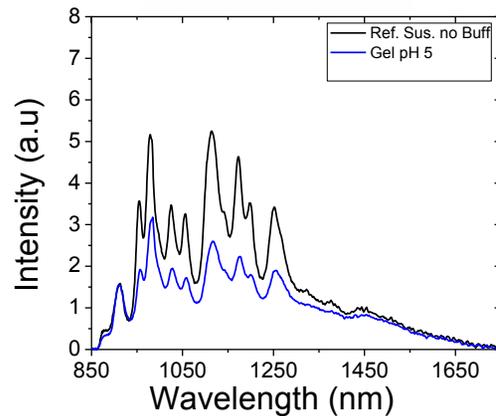
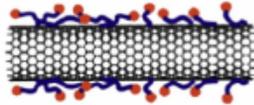
TPP



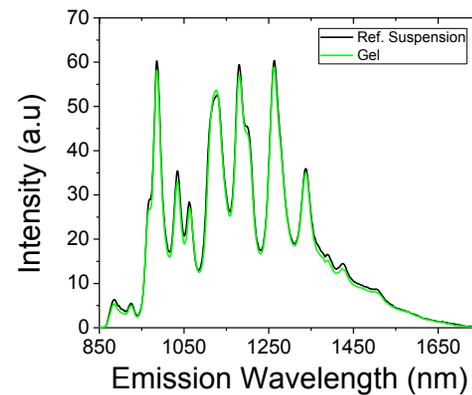
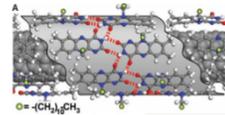
Unclassified

# Aerogel Requirements

## SDS

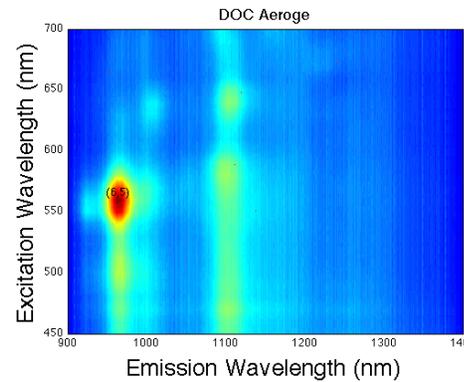
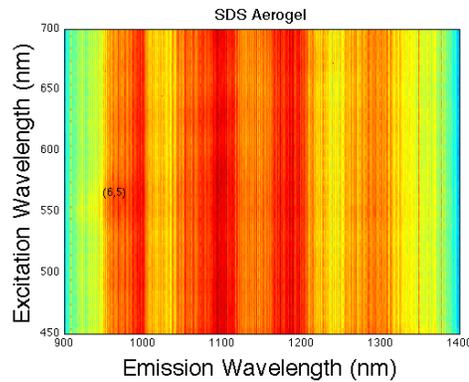


## DOC



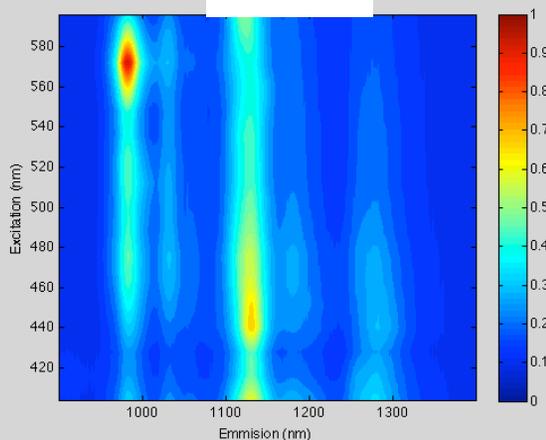
- Better SWCNT wrapping will result in better isolation from sol-gel and maintain better optical properties

## AEROGEL

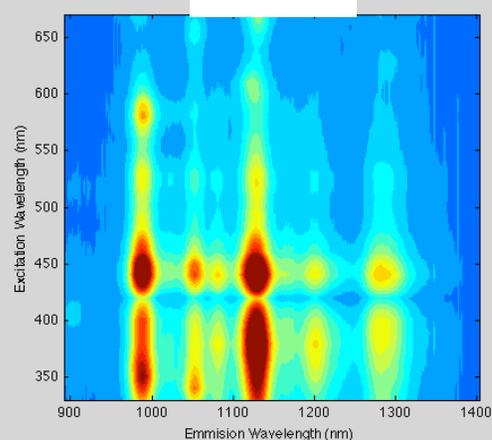


# Various Surfactant

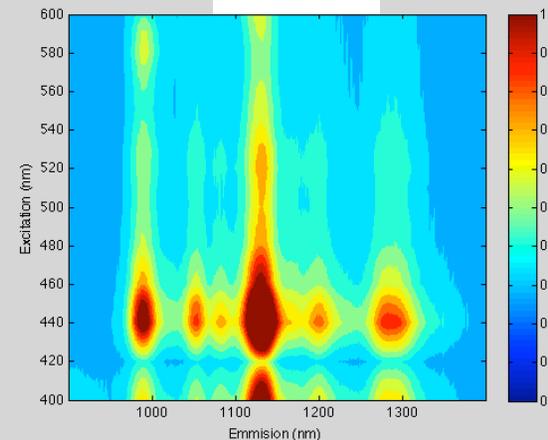
DOC



SDS

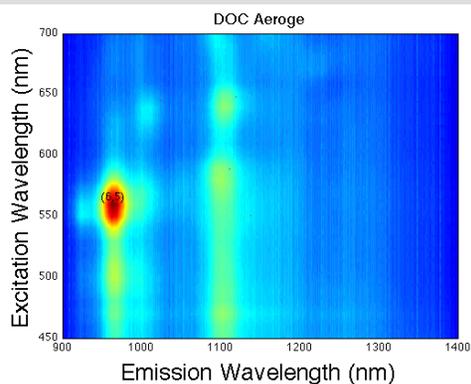


SDBS

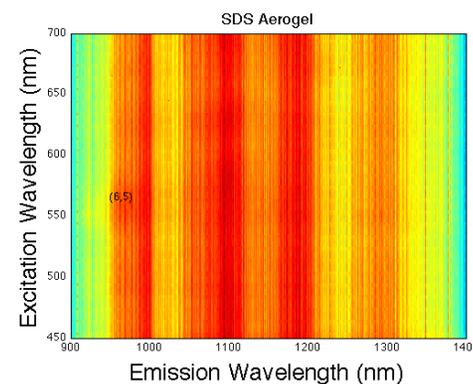


Requires greater heating for minimal transfer.

## AEROGEL

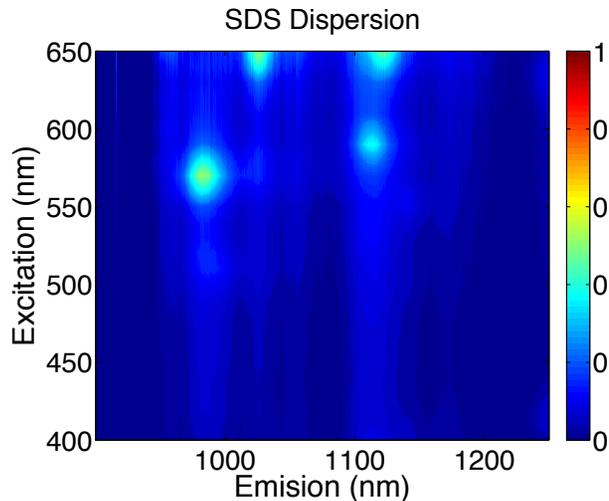


Strong transfer in both SDS and SDBS; Porphyrins need a more accessible wrapping, which will not maintain fluorescence in aerogel.

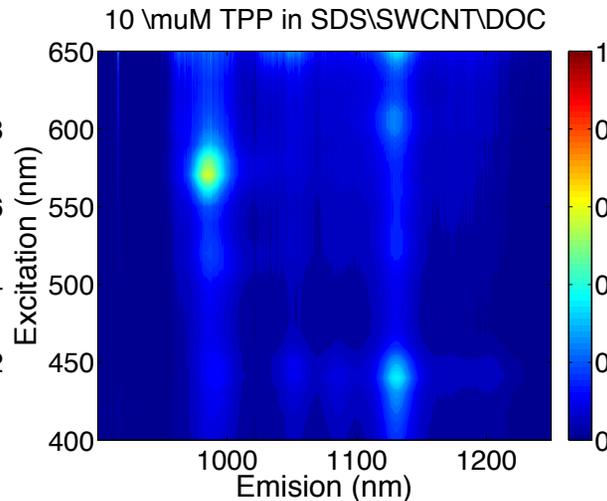


# Energy Transfer in Aerogel

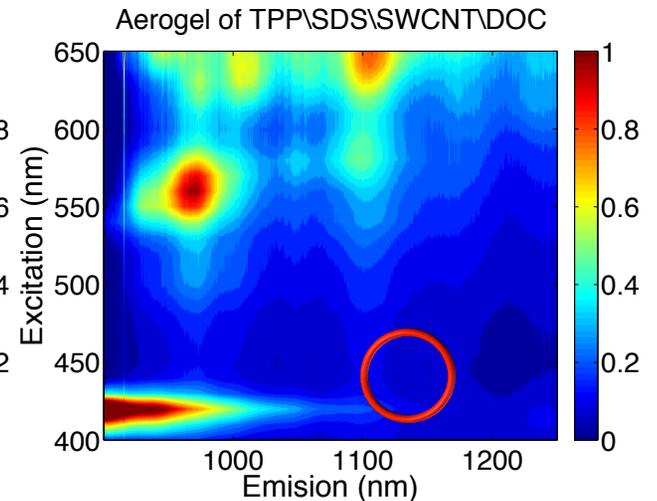
## SOLUTION



## WET GEL



## AEROGEL

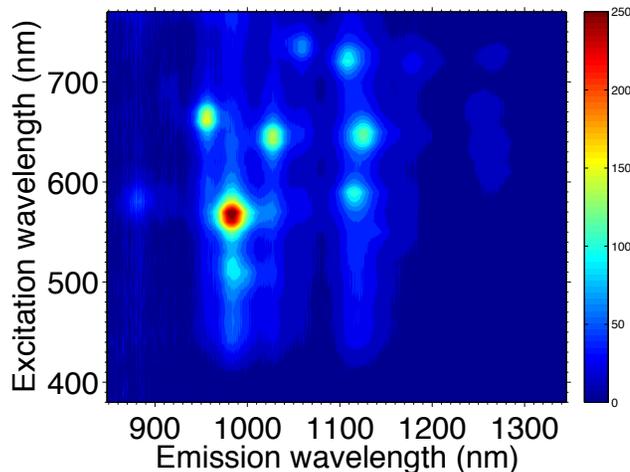


- Free porphyrin remain trapped in aerogel and no presence of energy transfer.
  - Have porphyrin been removed during aerogel process?
  - Are the present but in a dried configuration no longer fluoresce?
  - Without solvent, are the porphyrin no longer in energy transfer configuration and now only fluoresce as free porphyrin?

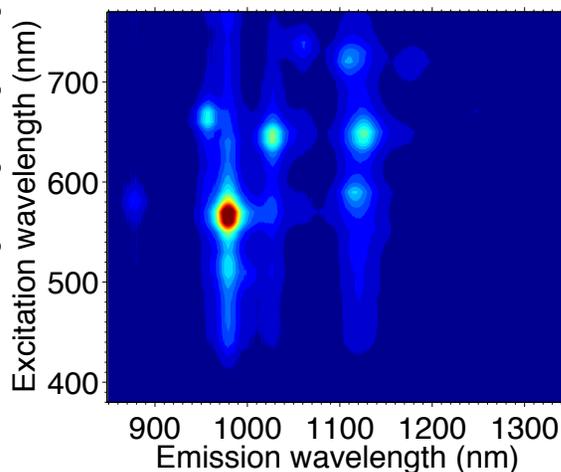
# Porphyrin Gels

## SOLUTION

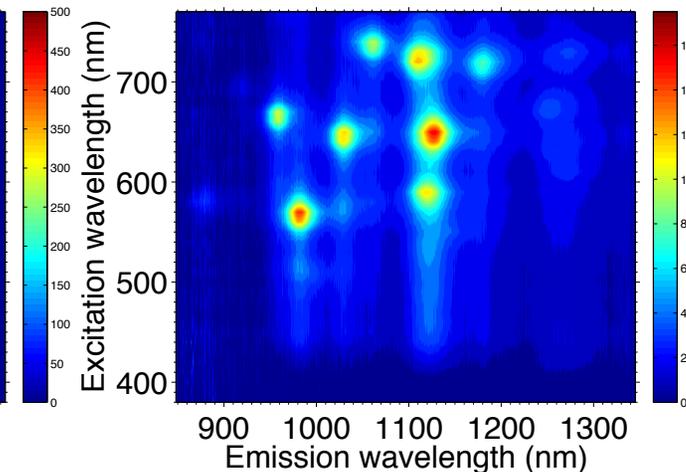
1% SDS with SWCNT in DOC



2% SDBS with SWCNT in DOC

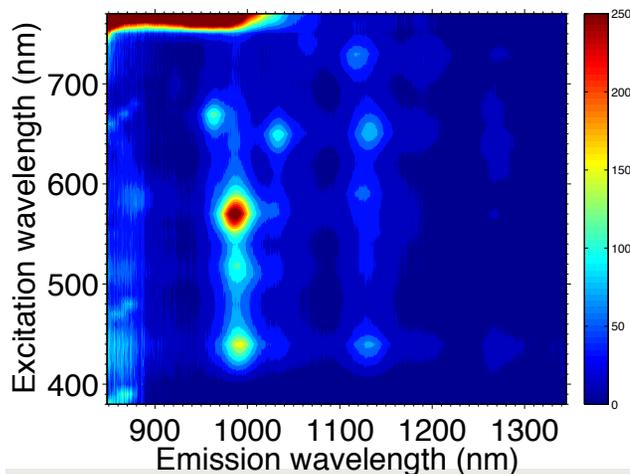


1% TWEEN80 with SWCNT in DOC

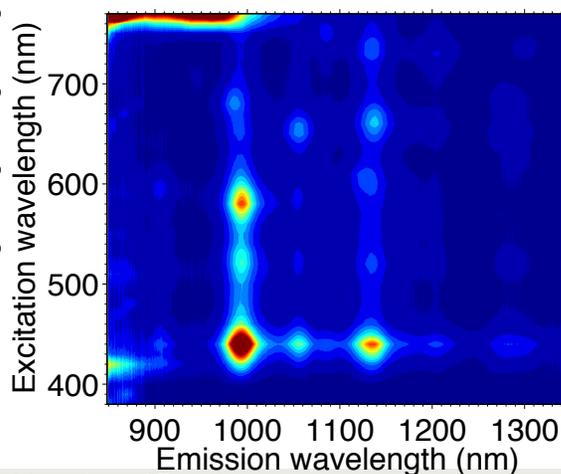


## WET GEL

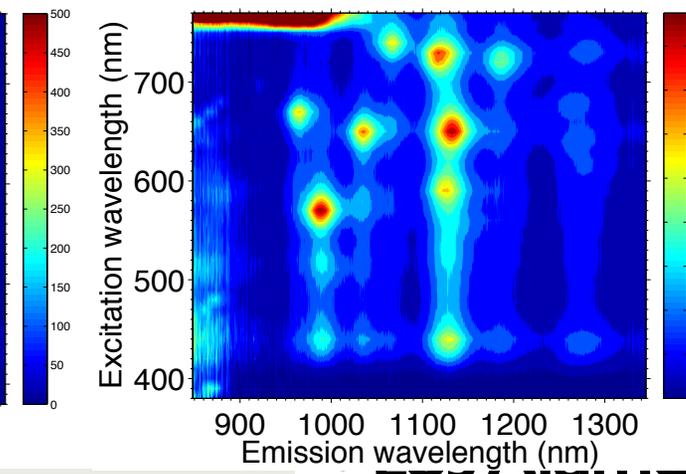
5 $\mu$ M TPP in 1% SDS\SWCNT\DOC



5 $\mu$ M TPP in 2% SDBS\SWCNT\DOC



5 $\mu$ M TPP in 1% TWEEN80\SWCNT\DOC

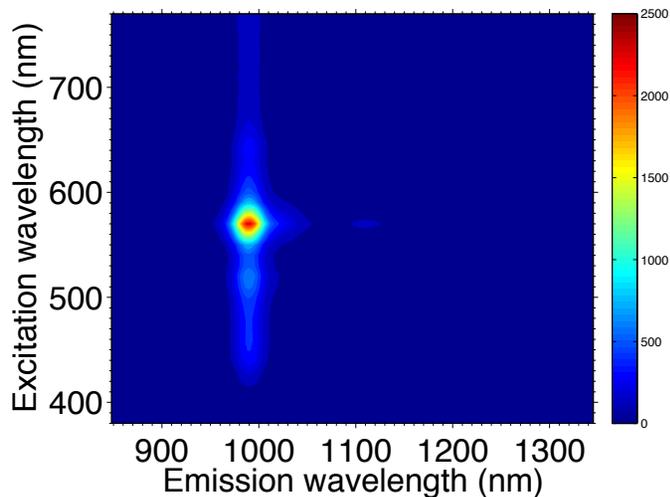


Unclassified

# Energy Transfer in Separated SWCNTs

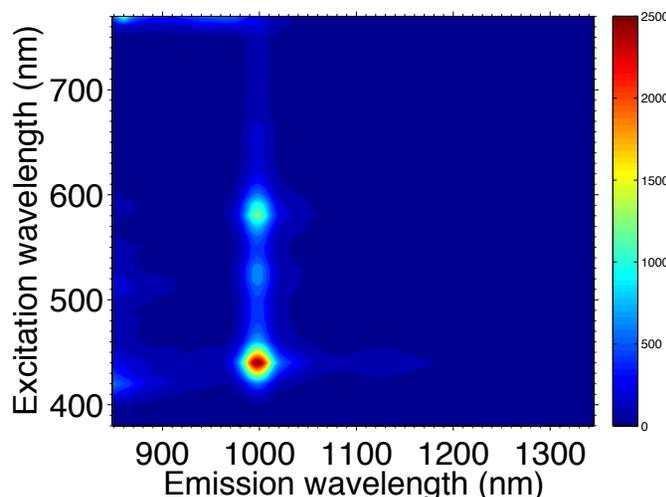
## SOLUTION

ATP Separated (6,5)



## WET GEL

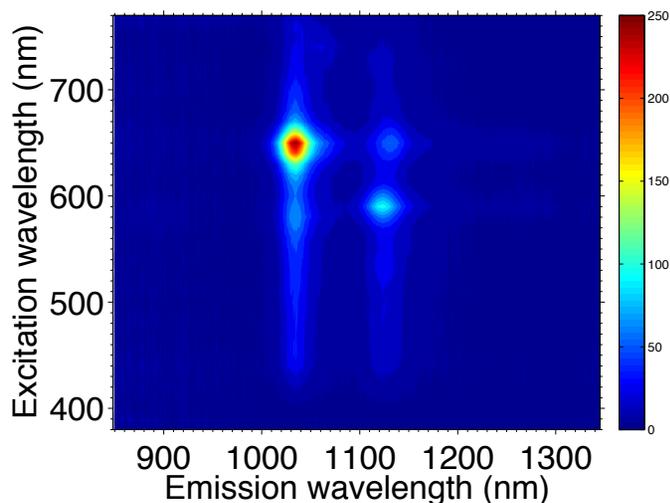
Energy Transfer in (6,5) Gel



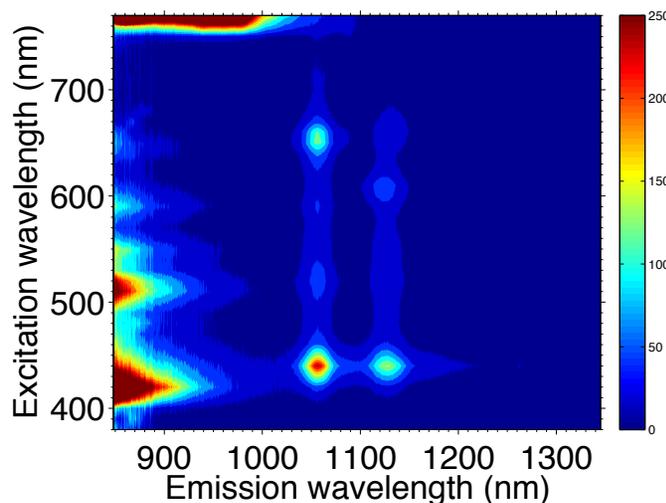
- DOC dialyzed ATP separations exhibit strong energy transfer maintained in wet gel state.

- First step toward energy transfer analysis in solvent free environment.

ATP Separated (7,5) & (8,4)



Energy Transfer in (7,5) & (8,4) Gel



- Free porphyrin emission when excited at 420nm

- SWCNT associated porphyrin emission when excited at 450nm

# Summary

- Surfactant acts to both stabilize porphyrin and transport porphyrin to SWCNT surface
- Evidence of strong energy transfer between TPP and SWCNTs
  - TPP absorption shift from 420 nm to 450 nm suggesting  $\pi$ -stacking
  - TPP fluorescence mostly quenched
  - SWCNT fluorescence at porphyrin absorption
  - Intrinsic SWCNT fluorescence red-shifts from change in local environment
- Incorporation into silicon wet gels while maintaining energy transfer
  - Need to develop a technique to maintain transfer in aerogel state

# Questions!

Unclassified